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The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY

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Abstract—The biogeochemical cycling of elemental Hg has important effects on the global and regional mobility and reactivity of the metal, and has not been well characterized in coastal marine systems. Five sets of measurements examining the spatial/temporal distribution of dissolved gaseous Hg (DGM), total Hg (Hg_T), and reactive Hg (Hg_R) in the waters of Long Island Sound (LIS) indicate that Hg^o evasion is geochemically significant, and an estimated 35% of the total annual Hg inputs to the system (average flux: 342 pmol m^{-2} d^{-1} to the atmosphere, based on a gas exchange model). DGM concentrations ranged from 0.04 to 0.55 pM (81–1167% saturation relative to atmospheric equilibrium), and show maxima in the surface mixed layer. Distinct seasonal patterns were observed, including higher DGM concentrations and percentage saturations during the warmer months. Seasonally averaged unfiltered Hg_T concentrations decreased by an order of magnitude from western LIS to the east, whereas the percent of unfiltered total as Hg_R increased from 14% in the west to 71% in the east. Relationships between filtered Hg_R, DOC, and DGM suggest that the DGM distribution within LIS is related to the supply and distribution of labile Hg reactant, which is in turn controlled by the distribution and nature of DOM. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

The biogeochemical cycling of mercury has been relatively well characterized for fresh water lakes and terrestrial watersheds (Fitzgerald et al., 1991; Vandal et al., 1995; Hudson et al., 1994; Watras et al., 1995; St. Louis et al., 1995; Rudd, 1995; Hultberg et al., 1995), but less is known about the processes and pathways that partition and transport the metal in coastal and estuarine systems (Cossa and Gobeil, 2000; Mason et al., 1999; Horvat et al., 1999; Quemerais et al., 1999; Mason et al., 1993; Stordal et al., 1996; Amyot et al., 1997; Bloom et al., 1999). The inflow of watershed and urban waters likely extends the cycling of terrestrially derived Hg into coastal zones, which are modified by a unique set of chemical, biological, and physical constraints (e.g., salt, marine organisms, estuarine and tidal mixing, sedimentation; Fitzgerald et al., 2000)

Research aimed at determining the fate and reactivity of Hg in coastal waters is gaining national attention, as concerns over regional recreation, fisheries, and human health impacts are becoming management priorities [consumption advisories by the World Health Organization (1990), USEPA, and 40 states; U.S. EPA, 1998a]. Consequently, research must focus on the spatial and temporal distribution of Hg species in coastal waters, sources of labile Hg, production mechanisms for monomethyl (MeHg) and elemental Hg (Hg^o), and relative importance of fluxes to regional budgets. A companion mass balance study examining Hg distributions and fluxes in Long Island Sound, CT (LIS; a temperate estuary) has recently been completed, allowing for refinement of these research topics and improvement upon previously qualitative characterizations (Fitzgerald et al., in press).

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1.1. Dissolved Gaseous Mercury

The aqueous biogeochemical formation of elemental Hg in the coastal zone is of particular interest, for it is a mechanism for removal of Hg from surface water to the atmosphere, and may compete for labile Hg(II) substrate with the methylation process (Fitzgerald et al., 1991). Sources of this substrate to coastal systems include both natural and anthropogenic components (Mason et al., 1994), which enter via atmospheric deposition (Lamborg et al., 1995), waste water treatment facilities, industrial discharges (Lindberg and Stratton, 1998), exchange with continental shelf waters, and riverine inputs (Fitzgerald et al., in press).

Studies conducted on the Great Lakes and terrestrial seepage lakes have indicated that Hg^o evasional fluxes can be as great as 50% of the total annual Hg input to the system (Mason and Sullivan, 1997; Fitzgerald et al., 1991; Watras et al., 1995), and it is possible that similar behavior may be occurring in coastal regions. Mason et al. (1999) report that Hg^o evasion constitutes 10 to 15% of total inputs to Chesapeake Bay. Other work on the St. Lawrence River shows that although evasion occurs at rates similar to those observed in lakes, it represents a relatively small component of the total Hg input ($<0.2\%$) due to the short hydraulic residence time of the system (Quemerais et al., 1999). Modeling of the global Hg budget indicates that Hg^o evasion from the surface ocean may be equal in magnitude to for all of the direct deposition to the system (10 Mmol), and account for roughly 30% of total annual emission to the atmosphere (Mason et al., 1994).

Several Hg(II) reduction mechanisms have been experimentally observed, including photochemical reduction in fresh (Amyot et al., 1994; Lindberg et al., 1995; Xiao et al., 1991, 1995) and marine waters (Costa and Liss, 1999; Amyot et al., 2000, 1997), electron transfer from organic material (Alberts et al., 1974; Skogerboe and Wilson, 1981; Allard and Arsenie,

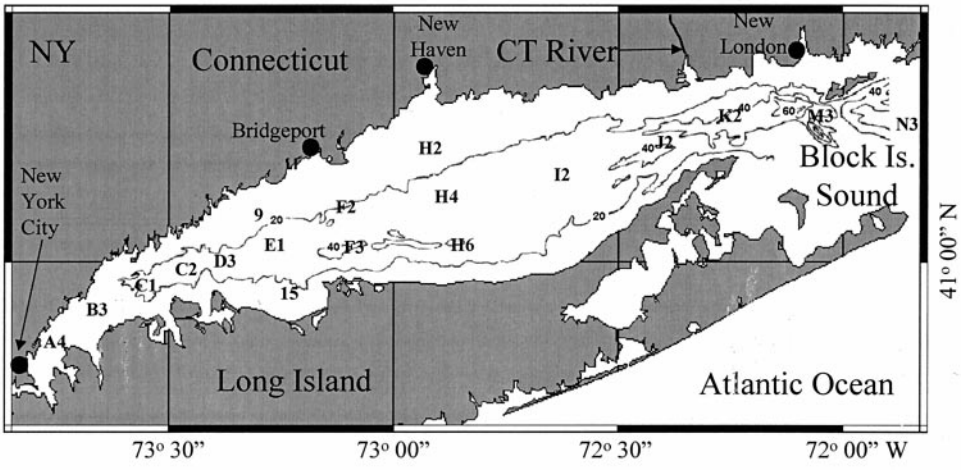

Fig. 1. Bathymetry and CT DEP station locations for Long Island Sound. Most of the bottom of LIS is gently sloping towards Long Island, NY, with an average depth of 21 m. The eastern Sound is narrow and deep, with significant tidal flow to and from Block Island Sound.

1991), and biological mediation by phytoplankton (Ben–Bassat and Mayer, 1977, 1978; Mason et al., 1995) and bacteria (Barkay et al., 1989; Ji et al., 1989).

Elemental Hg in natural waters is measured as part of the operationally defined fraction "dissolved gaseous Hg" (DGM), which includes both of the readily volatile species, Hg^o and dimethyl Hg (DMHg). DMHg is not detected in the surface waters of Long Island Sound (LIS), as observed from 10 samples collected from surface waters along the entire central axis of LIS during June, 1996 (G. Vandal, unpublished data). Detectable DMHg concentrations are not observed in the surface waters of the Equatorial Pacific, North, and South Atlantic Oceans, or the North Sea (Mason and Fitzgerald, 1993; Mason et al., 1998; Mason and Sullivan, 1999; Baeyens and Leermakers, 1998); it is therefore inferred that measures of DGM in the surface waters of LIS are reliable representations of the ambient Hg^o concentration.

Elemental Hg has been measured in fresh and marine waters to all depths, using a variety of purge/trap and floating box techniques (Kim and Fitzgerald, 1986; Xiao et al., 1991). Concentrations are almost always at or above that set by atmospheric equilibrium (typically 0.04–0.10 pM for LIS; Sanemasa, 1975), suggesting that in situ processes are responsible for the production of Hg^o. Oxidation of Hg^o has recently been shown to be of geochemical importance in high-chloride waters and in the dark (Amyot et al., 1997), which competes against processes forming Hg^o. The ramifications of oxidation include analytical artifacts (decreasing sample DGM during extended storage) as well as decreased evasion to the atmosphere relative to the amount of Hg^o actually produced by reduction mechanisms. Thus, our DGM measurements are interpreted as the net result of *net* redox processing and gas exchange.

1.2. Study Region

The Long Island Sound estuary is a highly impacted coastal region characterized by large metropolitan centers, a large watershed drainage area, and mixing with Block Island Sound and the East River at its eastern and western ends, respectively (Fig. 1). The presence of a sill in western LIS creates counterclockwise gyre flow in the central sound. In the east, the Connecticut River (CTR) supplies 70% of the fresh water to LIS annually, and over 90% of the flow during the spring melt period (February–May; USGS, 1994). This freshwater input flows eastward into Block Island Sound and westward into LIS in an oscillating fashion (as two-layer flow), with a magnitude estimated to be the same order of magnitude as the CTR outflow (O'Donnell, personal communication). Despite this riverine influence, surface salinity generally increases towards eastern LIS; only the sampling stations immediately offshore from the CTR mouth exhibit salinities lower than their surroundings. Although the contribution of water to LIS from the East River is smaller than that of the Connecticut River (and also not well constrained), its potentially elevated Hg concentration and anthropogenic contributions may have significant regional influence on the Hg content and speciation dynamics of western LIS. The Sound ranks sixth in the United States for estuary surface area (3200 km^2), third in water volume (6.2×10^{10} m^3), and nineteenth in land drainage area (44,700 km^2; National Oceanic and Atmospheric Administration, 1985).

This work examines the hypotheses that: (1) DGM distributions within LIS are spatially and temporally variable due to the distribution of precursor Hg(II) and the mechanisms of DGM formation; and (2) that Hg^o evasion constitutes a significant fraction of the annual Hg budget of the Sound. This study was conducted in association with a detailed and comprehensive research program aimed at determining Hg fluxes, reactions, and distributions within LIS (Fitzgerald et al., in press).

2. METHODS

2.1. Experimental Design

Spatial and temporal distributions of DGM, unfiltered reactive Hg (Hg_R), and total Hg (Hg_T) were measured in LIS during five research cruises between August 1995-October 1997. Filtered Hg_R and Hg_T were measured only during the August 1995 and October 1997 cruises. The August 1995 collection examined Hg species in both the vertical

and horizontal, while the other cruises focused on surface waters only (0–2 m depth). The May 1997 cruise sampled surface stations, as well as station N3 at two depths. Sampling locations were chosen to give even spatial coverage, in association with existing Connecticut Department of Environmental Protection Water Quality Program (CT DEP) collection sites (18 along the axis of LIS, with several others periodically sampled; see Fig. 1). Ancillary data for each collection [salinity, temperature, Chl *a*, dissolved organic carbon (DOC), and total suspended solids (TSS)] were obtained from the CT DEP, to assist in elucidating Hg^o production mechanisms. Sample cruises included all four seasonal conditions, such that an annual evasional estimate could be made.

2.2. Water Sampling

Water was sampled from LIS using two methods. Surface samples were collected using a plastic pole with a Teflon™ bottle attached to its end, whereas deeper samples were obtained by using an 8-L, Teflon™-lined, acid cleaned Niskin bottle (General Oceanics Co. "Go-Flo™") that was attached to a weighted Kevlar™ hydrowire. Standard trace metal-free clean techniques (Patterson and Settle, 1976; Fitzgerald, 1999) were practiced at all times, with special attention paid to the orientation of the ship and wind direction to avoid contamination. The surface sampler was a 2.5-m PVC pipe with a 2.5-L Teflon bottle attached using cable ties, which was dipped directly into the water from the deck of the CT DEP vessel *R/V John Dempsey*. The pole was submerged quickly so as to avoid sampling the surface microlayer; this does not seem to be a concern, as surface samples collected using Go-Flo™ bottle that was opened below surface agree well with manual collections. Care was taken to keep particles away from the sample bottles while they were exposed to the atmosphere (ship's stack gases, clothing, etc.). Teflon™ bottles were stored containing 500 mL of 1% HCl (v/v), which was discarded just before sampling. After attachment to the pole, the bottle cap was removed and the bottle rinsed (shaken) three times with sample before collection.

Deeper samples (3–35 m) were decanted into 2.5-L Teflon™ bottles from a Go-Flo™ bottle that was sent to depth with open ends, and tripped closed with a Teflon™ messenger. Generally 6 L of sample were collected from each bottle cast. Care was taken not to agitate the samples excessively, which may alter its dissolved gas content.

After collection, bottles from both methods were capped and placed into double bags; bottles were stored in coolers under ice until delivery to the University of Connecticut laboratory, where they were analyzed immediately for DGM. Total Hg samples were acidified to 1% HCl (v/v) upon arrival, whereas Hg_R samples remained unacidified until just before analysis.

2.3. Analytical

Details on the analytical methods for Hg species (Hg^o, Hg_R, Hg_T) in water samples may be found in Bloom and Crecelius (1983), Fitzgerald and Gill (1979), Kim and Fitzgerald (1986), Bloom and Fitzgerald (1988), Mason et al. (1993), and Mason and Fitzgerald (1993). Briefly, Hg_T was determined by chemically oxidizing the sample with BrCl for several hours, followed by reduction to volatile Hg^o by using $SnCl_2$ and subsequent trapping onto Au columns. Traps were then thermally desorbed and analyzed by using cold vapor atomic fluorescence spectrophotometry (CVAFS). Reactive Hg is an operationally defined measurement where the sample is acidified just before analysis (within 30 min), and is identical to the Hg_T procedure without the chemical preoxidation step (Hg_R includes DGM and species reduced by $SnCl_2$, such as inorganic Hg complexes and weaker organic associations). This work refers to "labile Hg" in the discussion as a broad nonoperationally defined category that may overlap the Hg_R fraction, but is theoretically based upon its ability to be methylated and/or assimilated into biota. Discussions of Hg_R findings in the literature have led to questions about its interpretation (Bloom, 1994), due to the fraction's dependency upon storage time, pH, and uncertainty over exactly which species are being detected. Although these caveats are not directly addressed in this work, the Hg_R data were obtained by using identical procedures throughout all collections, and samples are interpreted relative only to others within this study. Filtered fractions were obtained immediately upon collection by passing samples through pre-ashed quartz fiber filters (nominal 0.7 μm; placed in Teflon filter pack). Reactive and total Hg were measured within 2 days of collection, and kept refrigerated until analysis.

Dissolved gaseous Hg was measured immediately (within 4–6 hr) after arrival at our laboratories to avoid any Hg^o gain/loss associated with degassing, temperature change, Hg^o oxidation, or further reduction. No observable oxidation has been observed in our samples, as 2-day storage of bottles refrigerated in the dark showed no statistical concentration difference from samples that were immediately analyzed (*t*-test; $p > 0.25$; $n = 3$). Further, comparisons of instantaneously measured DGM in LIS water versus identical samples analyzed several hours later in the laboratory show no consistent evidence of DGM loss during storage (W. Fitzgerald, unpublished data). Two liters of sample were slowly decanted into acid-cleaned glass aspirators, and purged with ultra-pure N_2 for 30 min at 1 L min^{-1} through a glass frit. The aspirator was purged with N_2 for 5 min before sample addition to remove Hg^o associated with room air. The gas stream was passed through a Teflon soda lime column, collected on Au traps that were dried for 1 min using N_2, and thermally desorbed into an atomic fluorescence spectrophotometer (Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988).

2.4. Calculation of % Hg^o Saturation

The solubility of dissolved elemental Hg was estimated for pure water using the Henry's Law constant (H) and the ideal gas law:

$$P_{Hg^o} \approx n_{Hg^o}(RT)/V$$

$$H_{Hg^o} = \frac{P_{Hg^o}}{X_{Hg^o}}$$

$$[Hg^o]_{EQ} = X_{Hg^o}(55.5 \text{ mol } H_2O \text{ } L^{-1})$$

$$\% \text{ Saturation} = \frac{[Hg^o]_{Measured}}{[Hg^o]_{EQ}} \times 100$$

where P_{Hg^o} = atmospheric partial pressure for Hg^o, T = temperature (^{o}K), n_{Hg^o} = moles Hg^o per volume air, R = gas constant (8.314 J K^{-1} mol^{-1}), V = volume of air (L), and X_{Hg^o} = mole fraction of Hg^o in water. The Henry's Law constants for Hg^o in seawater were calculated after Sanemasa (1975):

$$\log H = \frac{-1078}{T} + 6.25$$

for pure water, and equilibrium concentrations were decreased to account for the effects of ionic strength on solubility (11% for 35 psu seawater), and were linearly adjusted for the salinity of the samples (Sanemasa, 1975). Mean aqueous Hg^o concentrations calculated to be in equilibrium with the atmosphere are presented for five seasonal cruises in Table 5, by using average salinity, water temperature, and atmospheric total gaseous Hg concentrations.

3. RESULTS AND DISCUSSION

3.1. Quality Assurance

Seasonal sampling of LIS was conducted with duplicate analysis of Hg species in approximately 12% of the collections, and in 19% of the DGM samples. Procedural blanks were performed before and during each analysis. The detection limit for CVAFS analysis of DGM, Hg_R, and Hg_T was 0.07, 0.23, and 0.17 pM, respectively. A summary of the quality assurance results for the analysis of LIS samples using the purge/trap/CVAFS technique is presented in Table 1. Gold-coated columns were tested before each analysis to determine Hg^o trapping efficiency, whereas procedural spike recovery was determined before every third analysis (by injecting known masses of Hg^o standard into a port located just before the aspiration frit).

Table 1. Quality assurance summary for the analysis of DGM and Hg_R in sea- and river water using the purge/Au-trap/CVAFS technique.

Analyte	Sample column spike recovery (%)	Procedural spike recovery (%)	Survey sample aspirator blank (pmol)	Method precision (% RSE)
Detector mean ± SE	99.9 ± 2.6			
n	20			
DGM mean		99.4 ± 4.8	0.11 ± 0.008	9.5 ± 2.3
n		15	8	18
Hg_T mean		98.7 ± 2.6	0.17 ± 0.005	5.9 ± 1.0
n		9	14	6
Hg_R mean		104.7 ± 2.7	0.11 ± 0.01	4.8 ± 1.7
n		11	17	6

Relative standard error (% RSE) = SE/sample mean × 100.

3.2. LIS Ancillary, Hg_R, and Hg_T Survey

A summary of the mean Hg_R and Hg_T distribution for surficial waters from all five seasonal collections and stations is presented in Table 2. Mean unfiltered Hg_T concentrations lie within a range of 2.3 to 19.9 pM, whereas mean unfiltered Hg_R is between 1.3 to 4.5 pM. The unfiltered Hg_T concentration increases westward by nearly an order of magnitude; the average particulate Hg_T fraction increases from 32 (Station I2) to 88% of the total in far western LIS (Station A4). This is likely due to the significant loading of particulate and dissolved organic material from metropolitan New York municipal waste treatment facilities and surface runoff, which serve to strongly bind Hg (Farrow et al., 1986; Fitzgerald et al., in press). The distribution of total suspended solids generally increased by a factor of 2 to 3 from east to west for all periods except August 1995, where no trends were observed. Measures of DOC generally increased by a factor of two from east to west during every collection, with the exception of February 1996 where no change was observed. This is likely due to the elevated river inputs to LIS caused by an early spring snowmelt during this period. As particulate Hg was not measured during this study, direct estimates of partition coefficients are not available.

The particulate scavenging signature is apparent in the Hg_R values, as concentrations remain low relative to Hg_T; the unfiltered Hg_R fraction (as % Hg_T) is higher in the eastern Sound (Station H4-N3 mean ± SE: 59 ± 5%), than in the west (Stations A4-E1: 30 ± 7%). Such differences are also due to proximity to coastlines and the outflow of the Connecticut River (CTR), which is a principal source of labile Hg to eastern LIS (Rolfhus, 1998; this companion study posits that Hg becomes more "reactive" during estuarine mixing of Connecticut River waters, as Hg-terrestrial DOC complexes undergo ion exchange with major seawater cations, as well as the effects of marine DOC being generally weaker complexing agents for Hg than terrestrial DOC). Direct observations of increasing unfiltered Hg_R concentrations and incubation-derived net reduction rates seaward through the estuary has been documented (Rolfhus, 1998). These observations are consistent with the St. Lawrence Estuary (Cossa and Gobeil, 2000), where Hg_R/Hg_T ratios range from 8 to 59% in surface waters and average 20%.

Table 2. Summary of Hg speciation at LIS sampling stations.

Station	Max. depth (m)	Lat (°N)	Long (°W)	Unfilt HgT (pM)	Filt HgT (pM)	Unfilt HgR (pM)	Unfilt HgR/ unfilt HgT (%)	Filt HgR (pM)	Filt HgR/ filt HgT (%)
A4	36	40.87	73.74	19.9 ± 6.7	2.4 ± 0.1	2.7 ± 0.8	14	1.0 ± 0.4	42
B3	18	40.92	73.64	12.5 ± 5.6	3.9	1.7 ± 1.2	14	—	—
C1	21	40.96	73.58	8.0 ± 1.1	2.7	3.5 ± 1.6	44	0.8	30
C2	34	40.99	73.5	8.9 ± 0.1	—	1.8	20	—	—
D3	43	40.99	73.41	5.9	2.1	3.1 ± 2.0	53	1.5	71
E1	39	41.02	73.29	5.2 ± 1.3	3.2	1.8	35	1.2	38
9	9	41.07	73.34	11.8 ± 0.6	3.9	3.2 ± 1.0	27	3.5	90
15	15	40.93	73.22	7.7	—	—	—	1.6	—
F2	20	41.08	73.07	1.9	2.1	—	—	2.0 ± 0.3	95
F3	40	41.02	73.15	—	4.5	—	—	2.2	49
H2	16	41.18	72.96	—	3.2	—	—	4.3	134
H4	25	41.1	72.93	5.0 ± 1.3	4.3	2.0 ± 1.4	40	2.6 ± 0.5	60
H6	42	41.03	72.91	—	4.4	—	—	2	46
I2	28	41.14	72.66	5.6 ± 0.4	3.8	3.9 ± 1.3	70	2.4	63
J2	14	41.18	72.46	7.4 ± 3.3	2.7	4.1 ± 0.7	55	3	111
K2	37	41.24	72.27	7.6 ± 2.1	4.7	4.5 ± 0.6	59	2.8 ± 0.9	60
M3	29	41.24	72.05	3.5 ± 0.5	—	2.5	71	2.5	—
N3	42	41.23	71.86	2.3	—	1.3	57	—	—

Mean concentrations (±SE) for all five collection dates. "—" = not sampled.

Table 3. Summary of August 1995 vertical profile for unfiltered Hg species in LIS (total, reactive, and dissolved gaseous Hg.

Station (max. depth)	Depth (m)	Salinity (psu)	Unf HgT (pM)	Filt HgT (pM)	Unf HgR (pM)	Filt HgR (pM)	DGM (pM)
A4 (33 m)	1	27.0	13.4	2.3	0.1	0.6	0.29
	5	—	9.9	2.1	1.0	0.5	0.34 ± 0.02
	15	27.6	6.1	2.2	1.0	0.9	—
	30	27.7	12.1	3.0	3.9	2.0	0.18
C1 (18 m)	1	27.3	6.9	2.7	2.3	0.8	0.39
	5	—	9.3	5.5	1.2	0.4	—
	9	27.7	3.5	3.3	2.6	0.3	0.31
	15	27.9	3.2	4.0	1.7	0.4	0.24
E1 (38 m)	1	27.6	6.4	3.2	0.8	1.2	0.55 ± 0.03
	5	—	1.6	2.5[a]	0.3	0.9[a]	0.89
	15	28.4	3.9	3.4	3.3	1.1	—
	30	28.5	44.1	1.6	40.1	1.2	0.22
F2 (20 m)	1	28.1	1.9	3.4[a]	0.7	1.7[a]	0.45
	10	28.2	5.0 ± 0.5	1.8	1.0	0.4 ± 0.1	0.35
	15	28.6	13.8	6.6	4.1	2.3	0.16
H4 (23 m)	1	28.2	3.7	4.3	2.0	2.1	0.54
	10	—	5.3	2.3	2.4	1.4	—
	15	28.9	4.2	3.0	3.2	1.2	—
	20	29.1	8.6	3.1	3.0	2.6	0.29
K2 (38 m)	1	29.5	5.5	4.7	3.2	1.9	0.32 ± 0.01
	15	30.6	2.8	2.4	1.7	1.3	0.45
	30	30.6	3.0	3.9	3.0	2.2	0.47

"—" = not sampled. Error estimate is standard error of duplicate analyses. See Figure 1 for station location. [a] = possible filter contamination.

Filtered Hg_T and Hg_R fractions at the axial stations increase ca. two-fold west to east, likely due to the decreasing impact of particulate loads and the influence of the eastern CTR inflow. The filtered Hg_T/Hg_R ratio showed no distinct spatial trend (mean 68 ± 9%; Table 2), and indicates that filtered fractions are somewhat more labile than raw water samples. Particles may similarly be inhibiting bio-uptake of Hg species as the result of scavenging processes.

Vertical Hg speciation distributions (Hg_T, Hg_R, and DGM) were measured at six stations along the axis of LIS in August 1995, and are presented in Table 3. At each station, surface and near bottom depths were sampled, as well as depths bracketing the seasonal thermocline. The Hg_T and Hg_R data lack a consistent pattern, with some stations showing evidence of surficial riverine Hg_T influence (lower salinity at surface) and sedimentary sources at stations A4, E1, and F2 (supported by elevated relative TSS values at depth). A trend of increasing % unfiltered Hg_R/Hg_T towards the eastern end of LIS is observed in bottom waters, similar to that measured for surficial waters. Similar trends in the vertical were also observed in the St. Lawrence Estuary (Cossa and Gobeil, 2000), with enhancements in Hg_T and Hg_R in brackish surface waters and near the sediments, with lowest values in the intermediate zone. The authors suggest riverine and sedimentary sources, respectively.

The effect of DOC on the lability of Hg in surface waters was examined by considering Hg_R on filtered samples, which removes the effects of particles on complexation. Correlation coefficients for DOC vs. unfiltered Hg_T, unfiltered Hg_R, and % Hg_T (as Hg_R) were 0.15 or less for all collections, which is a predictable outcome given the variability that particulate material likely imposes. The filtered Hg_R fraction had the strongest correlation with DOC when the August 1995 and October 1997 data sets were combined ($r^2 = 0.45$; Fig. 2), suggesting that organic ligands are playing a prominent role in determining the (operationally defined) lability of Hg species in the surface waters of LIS. It is likely that specific fractions of the dissolved organic matter are controlling Hg reducibility (such as chelating or sulfur-containing marine organic matter), which may explain the relatively weak correlation to bulk DOC.

3.3. DGM Distributions

Results of the LIS seasonal DGM survey are found in Table 4, which includes surficial DGM concentration and calculated percentage of Hg^o saturation relative to atmospheric equilibrium. As mentioned, measured DGM concentrations reflect the competing contributions of Hg^o production rate and wind-

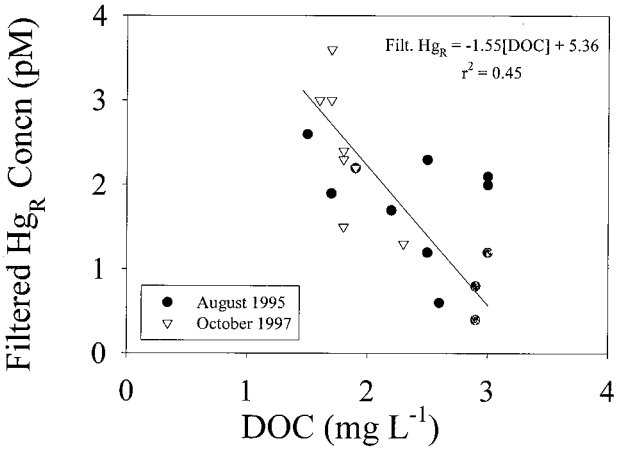

Fig. 2. Relation of filtered Hg_R concentration to DOC from the August 1995 (all depths) and October 1997 (surface only) sampling, which were the only collections for which filtered Hg_R was determined.

Table 4. Surficial DGM concentrations and corresponding percent saturation relative to atmospheric equilibrium (100% = equilibrium) from all collections.

	Feb 1996		May 1997		Aug 1995		Oct 1996		Oct 1997	
Station	DGM (pM)	Atm Sat. (%)	DGM (pM)	Atm Sat. (%)	DGM (pM)	Atm Sat. (%)	DGM (pM)	Atm Sat. (%)	DGM (pM)	Atm Sat. (%)
A4	0.20	219	0.10	134	0.29	572	—	—	0.075	146
B3	0.18	195	0.13	160	0.39	823	—	—	0.097	198
C1	—	—	0.15	199	—	—	—	—	—	—
C2	0.21	239	0.17	217	—	—	—	—	0.060[a]	122
D3	—	—	—	343	—	—	—	—	0.045[a]	93
E1	—	—	0.17	217	0.55 ± 0.03	1167 ± 5	—	—	—	—
9	0.24 ± 0.01	281 ± 15	—	—	—	—	—	—	0.11	243
F2	0.25	304	—	—	0.45	969	—	—	0.037[a]	81
H2	—	—	—	—	—	—	—	—	0.060[a]	136
H4	0.23	286	—	—	0.54	1161	—	—	0.13	305
H6	—	—	—	—	—	—	—	—	0.10	237
I2	0.27	351	0.23 ± 0.03	315 ± 44	—	—	0.25 ± 0.05	501 ± 90	0.089	203
J2	0.29	391	0.11	149	—	—	0.47 ± 0.09	942 ± 188	0.13	288
K2	—	—	0.12	166	0.32 ± 0.01	697 ± 20	0.27	546	0.18	416
M3	—	—	0.14 ± 0.003	190 ± 4	—	—	0.33 ± 0.09	666 ± 188	0.097	225
N3	—	—	0.19	248	—	—	—	—	0.16	373

Dashes represent stations not sampled. Error estimate is standard error of duplicate samples. a = less than method detection limit.

driven gas exchange. It is apparent from the surface water data that DGM varies significantly in space and time, with a grand mean and standard deviation of 0.20 ± 0.13 pM (n = 42). This corresponds to a mean saturation of 351 ± 267% for all surface sampling sites and dates, which is consistent with in situ Hg^o production. Only 5% (n = 2) of the surface samples were at concentrations below calculated atmospheric equilibrium (both from October 1997), whereas 70% were supersaturated by more than a factor of two. These values are consistent with Cossa and Gobeil (2000) and Amyot et al. (2000) who observed mean DGM concentrations of 0.22 ± 0.08 and 0.16 pM, respectively in the St. Lawrence Estuary. Mason et al. (1999) observed similar concentrations within Chesapeake Bay of 0.10 to 0.25 pM. The fraction of Hg_T as DGM was 5.5 ± 8.4% (mean ± SD; n = 47), with the majority of the Hg present as Hg(II) and associated with particles. These results are also consistent with those of Cossa and Gobeil (2000) and Mason et al. (1999), who observed ratios ca. 5%. DGM concentrations within LIS were greater than that measured at the Connecticut River end member during every collection that both samples were analyzed (February 1996, October 1996, and May 1997, averaging 0.14 ± 0.02 pM), indicating that rivers are likely not supplying elevated DGM waters to the sound.

The DGM data exhibit seasonal variability, with the summer period generally highest in concentration. This is consistent with literature that has observed Hg reduction dependencies upon phytoplankton/bacterial activity (Mason et al., 1995) and photochemistry (Amyot et al., 2000, 1997; Costa and Liss, 1999). It should be noted, however, that significant inter-annual variability exists (October 1996 and October 1997), likely due to annual differences in wind field, river flow, and biological activity. The elevated concentrations and percent saturations during August 1995 are thought to be enhanced by an extremely hot, calm period before sampling that may have enhanced photochemical/biological production while inhibiting gas exchange.

East-west spatial trends are difficult to resolve in the data, though elevated DGM concentrations are observed near the CTR outflow in eastern LIS (stations I2, J2, and K2) during all collections except August 1995 (when maxima were observed in central LIS). Figure 3 shows surficial DGM data for the four collections that had adequate E-W spatial coverage plotted versus salinity (excluding the October 1996 sampling and stations east of the CTR outflow—M3, N3), and indicates that DGM concentrations generally increase eastward towards more saline eastern LIS (though the CTR outflow is located in the east, its effects on salinity are not large enough to significantly alter the eastward increasing gradient that is established by open ocean water and western LIS end members). Differences in the slopes of Figure 3 are due (in part) to the natural range of salinity within LIS at these collection periods, which can vary by 4 to 6 psu spatially at a given date. These trends are

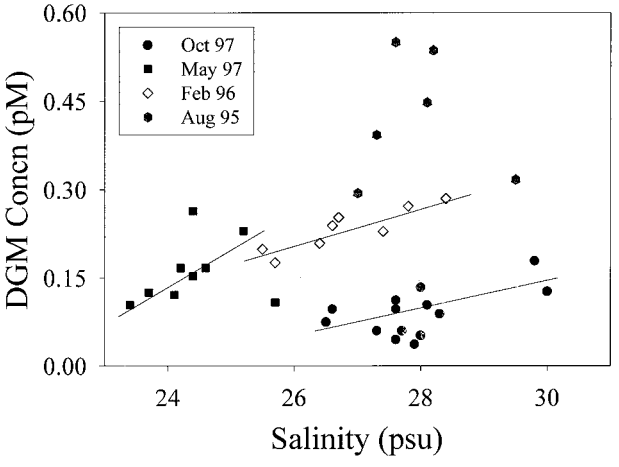

Fig. 3. Surface DGM versus salinity for all collections except October, 1996, where spatial E-W coverage was not sufficient. Stations M3 and N3 are not included, as they are east of the CTR outflow and do not follow the salinity relationship.

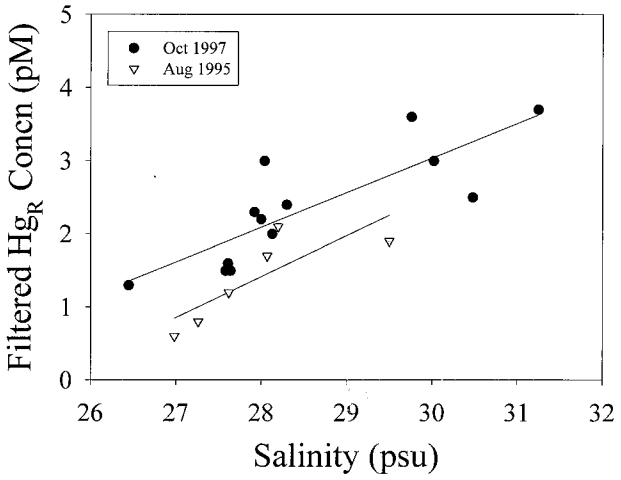

Fig. 4. Relation of filtered Hg_R to salinity for the two surficial collections in which the measurement was made: August 1995 and October 1997.

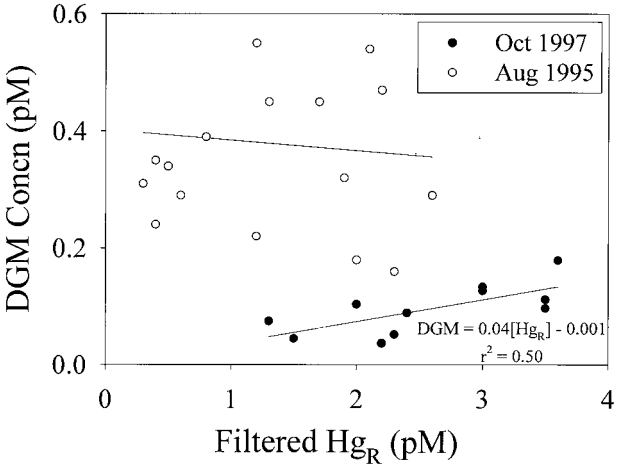

Fig. 5. Surface DGM versus the filtered Hg_R fraction for the two collections when filtered Hg_R was measured: August 1995 and October 1997.

consistent with the enhancement of percent unfiltered Hg_R (Table 2) and filtered Hg_R concentrations eastward (Fig. 4), and implies that both of the riverine Hg supply and low-DOC conditions characteristic of eastern LIS are contributing to DGM production.

Vertical DGM profiles were collected during August 1995 (entire LIS) and May 1997 (station N3 only; Table 3). Near-surface DGM maxima (0–10 m) are observed at 5 of 6 sampling sites. The exception is at Station K2, a high-energy region off of the Connecticut River Estuary where tidally induced vertical mixing may be homogenizing concentrations vertically. Stations A4 and E1 show slightly lower concentrations at the surface, which are possibly due to wind-induced gas exchange. These distributions are consistent with lacustrine DGM data (Vandal et al., 1995), where photochemical reactions are thought to be the predominant Hg^o production mechanism. The N3 station from May, 1997 shows that seawater from Block Island Sound (entering eastern LIS at the bottom of two layer flow) has DGM signatures within 5% of the surface water value (0.19 pM). This suggests that Block Island Sound is not an appreciable advective source of high-DGM water to the depths of eastern LIS, but data is limited. The presence of Hg^o supersaturations at depth suggests either that (1) it is produced in situ by microbial and/or abiotic processes; or (2) that Hg^o produced surficially is being mixed vertically by downwelling advection and diffusion; it is likely that a combination of both processes is occurring. The surficial maximum observations are consistent with Cossa and Gobeil (2000) in the St. Lawrence Estuary, who found relatively low DGM concentrations in bottom waters.

3.4. Inferred DGM Production Controls

Surface DGM was not well correlated with Hg_T and Hg_R fractions in most of the LIS samples, with the exception of the filtered Hg_R set collected in October 1997 (Fig. 5; $r^2 = 0.50$). This is the measured fraction that one might expect to best correlate with DGM, assuming that: (1) the reduction process is dependent on Hg(II) reactant that is composed of dissolved inorganic/organic Hg complexes; (2) that particulate Hg is generally unavailable for reduction; and (3) that reduction is substrate limited. This contention is supported by the work of Amyot et al. (2000), that observed pseudo-first order kinetics with regard to Hg(II) reactant and substrate limitation in photo-redox experiments. The August 1995 filtered Hg_R samples did not show a relationship with DGM (Fig. 5), which is likely due to the hot, still weather encountered during the sampling period (i.e., Hg^o was produced at rates faster than it was exchanged with the atmosphere). As mentioned, intense photochemical/biological activity coupled with low wind speeds likely account for these observations. Surficial DGM distributions did not correlate well with Chl *a*, and indicates that potential linkages between biological activity and Hg reduction are not well resolved.

3.5. Where is DGM Produced?

Although the salinity data (Fig. 3) suggest that the LIS DGM distribution is primarily dictated by the simple mixing of high-DGM eastern LIS water westward, dark seawater incubation experiments using Hg(II) spikes to 0.5 nM indicate that in situ processes are creating Hg^o at rates within a factor of two of each other at all locations along the LIS central axis (range 1.5–3.5% d^{-1} as Hg_T; Rolfhus, 1998).

Independent estimates of the residence time of Hg^o in LIS surface waters constrain whether the measured DGM is primarily formed in eastern LIS and advected westward, or if it is reflective of the reactant Hg(II) distribution:

1) *Production based calculation* (assuming a mean LIS Hg_T concentration of 6 pM, a 15 m mean annual mixed layer depth, a mean mixed layer DGM concentration of 0.20 pM, and that *all* Hg^o produced is evaded to the atmosphere): typical LIS reduction rates range from 1.5 to 3.5% d^{-1} (as Hg_T), which corresponds to 0.09 to 0.21 pM d^{-1} Hg^o production, or 45 to 105% d^{-1} of the mean,

ambient Hg^o concentration. This is equivalent to a Hg^o residence time of 2 to 10 days in the surface mixed layer.

2) *Evasion based calculation*: the mean estimated Hg^o flux based upon the gas exchange model of Wanninkhof (1992; ~350 pmol m^{-2} d^{-1}; see below), when averaged over the mixed layer depth, leads to a concentration decrease of 0.023 pM d^{-1}. This value corresponds to 12% d^{-1} of the mean ambient Hg^o concentration, or a residence time of 8.6 days.

Such rapid turnover of the Hg^o pool makes it is unlikely that a Hg^o signal (spatial pattern) produced only from Hg(II) reactant in eastern LIS would survive the period of westward mixing [estimated at 1 to 3 months; lower and upper bounds based upon a tidal residual of 5 cm s^{-1} (O'Donnell, personal communication) and ^{222}Rn measurements (Torgersen et al., 1997), respectively]. If the average mixed layer Hg^o residence time were 5 days, it would be recharged and evaded 6 to 18 times before fully mixing east to west in LIS.

Thus, the mixing and formation of labile Hg throughout LIS with concurrent in situ production is the more plausible explanation. This contention is supported by the relationship between filtered Hg_R and DGM in October 1997 (Fig. 5), which supports the "substrate hypothesis" put forth by Fitzgerald et al. (1991) stating that all important aqueous reactions compete for and are dependent upon the labile Hg(II) concentration. The distribution of labile Hg, in turn, is partially determined by the distribution of DOC (Fig. 2), which increases from east to west. The residence time of the filtered Hg_R fraction in October 1997 with evasion as the only biogeochemical sink was estimated at 107 d, assuming a mean filtered Hg_R concentration of 2.5 pM, a mean evasional flux of 350 pmol m^{-2} d^{-1}, and a mixed layer depth of 15 m. As particle scavenging and methylation constitute additional sinks, this value is likely an upper bound to the residence time. It is, however, on an order similar to the mixing time of LIS surface waters, and may allow for the spatial patterns observed for Hg_R in the sound. It is likely that the distribution of labile Hg(II) reactant distribution is a combination of three processes: (1) supply and mixing from principal riverine sources (mainly from the CTR Estuary); (2) pseudo-equilibrium with DOM and its distribution; and (3) consumption by Hg^o production and particulate scavenging. Although more sample collections are required to verify the relationships, we suggest that the observed DGM concentration is composed of Hg^o produced *locally* from labile Hg(II) reactant of riverine and atmospheric origin during the 1 to 2 weeks before collection.

3.6. Modeling Hg^o flux from LIS

The efflux of Hg^o from the surface waters of LIS to the atmosphere was modeled to assess its importance relative to other significant fluxes: watershed inputs, direct deposition, waste water treatment facilities (WTF's), tidally induced advection, and sedimentation. Three gas exchange models were used to provide a range of Hg^o evasional flux estimates for LIS, derived from the seasonal surface DGM data, measures of wind speed, water temperature, salinity, atmospheric total gaseous Hg concentration (TGM), and estimates of the Henry's Law constant for Hg^o. Wind speeds were used to determine a transfer ("piston") velocity for the removal of Hg^o from surface water, assuming that surficial wind stress is the dominant mechanism for creation of near surface turbulence in most oceanic situations (Asher and Wanninkhof, 1998). Relationships were used from:

1) Liss and Merlivat (1986):

For mean winds 0–3.6 m s^{-1}: $k = 2.8 \times 10^{-6} [0.17\,\bar{u}][Sc_{Hg^o}/600]^{-2/3}$

For winds 3.6–13 m s^{-1}: $k = 2.8 \times 10^{-6}[2.8\,\bar{u} - 9.6][Sc_{Hg^o}/600]^{-1/2}$

where k is transfer velocity for Hg^o (m s^{-1}), $\bar{u}^2$ is the mean windspeed (m s^{-1}), and $Sc_{Hg(o)}$ is the Schmidt number for Hg^o (Sc; defined as the kinematic viscosity of the liquid medium divided by the diffusion coefficient of the gas) normalized to the Sc for CO_2 in fresh water (600 at 20°C). This relationship is the simplest, and is derived from experimental measurement of SF_6 evasion from a fresh water lake in New York State (Wanninkhof et al., 1985).

2) Wanninkhof (1992):

$$k = 0.31\,\overline{(u^2)}\,[Sc_{Hg^o}/660]^{-1/2}$$

where k is transfer velocity for Hg^o (cm hr^{-1}), $\overline{(u^2)}$ is the mean squared wind velocity (m^2 s^{-2}), and the last term is the Schmidt number for Hg^o normalized to that for CO_2 in seawater at 20°C (660). This relationship originates from empirical wind speed data used to estimate the invasion of bomb-derived $^{14}CO_2$ into global surface waters, and is applicable to areas of steady winds and for short-term shipboard measurements. Modeling has revealed that k is proportional to $Sc^{-1/2}$ for an interface with waves (Coantic, 1986), and approaches $Sc^{-1/3}$ at elevated wind speeds (Asher et al., 1996). The Wanninkhof model is currently the most widely accepted method for determining wind-induced gas exchange fluxes, and is the model used to report Hg^o fluxes for comparison to other sources/sinks within the LIS Hg budget (Fitzgerald et al., in press).

3) Asher et al. (1995):

$$W_A = \overline{u^{3.41}}[3.96 \times 10^{-7}]$$

$$k_{o_2}, = 0.023[W_A] + 3.0 \times 10^{-5}$$

$$k_{Hg^o} = k_{o_2}[Sc_{Hg^o}/Sc_{o_2}]^{-1/2}$$

where W_A is the areal percent whitecap cover of the sea surface, based upon $\overline{u^{3.41}}$, the mean exponent of the wind speed (m s^{-1}); the transfer velocity k_{o_2} (m s^{-1}) for oxygen is linearly related to W_A. The transfer velocity for Hg^o (m d^{-1}) is corrected for the Schmidt number of oxygen (see Wanninkhof above). This model represents an improvement over the Liss and Merlivat model due to its incorporation of whitecapping and bubble plumes (experiments were carried out on several gases in a swimming pool with an oscillating paddle), but the calculated transfer velocity is relatively insensitive to changes in wind speed within a range relevant for LIS (3–7 m s^{-1}).

Table 5. Summary of gas exchange model parameters and estimated Hg^o evasional fluxes for LIS seasonal surface water sampling.

Season	Average wind velocity $\bar{u}$ ($m\ s^{-1}$)	$\overline{u^2}$ ($m^2\ s^{-2}$)	$\overline{u^{3.41}}$	Average axial surficial DGM (pM)	DGM in atmos. equilibrium (pM)	TGM ($ng\ m^{-3}$)
Winter (Feb. 1996)	4.5	26	400	0.23	0.08	2.8
Spring (May 1997)	6.4	48	1010	0.17	0.07	3.0
Summer (Aug 1995)	3.1	14	150	0.42	0.05	3.3
Fall (Oct 1996)	4.5	28	600	0.26	0.05	3.0
Fall (Oct 1997)	3.6	16	190	0.10	0.05	3.0

Season	Liss and Merlivat k ($m\ d^{-1}$)	Wanninkhof k ($m\ d^{-1}$)	Asher et al. k ($m\ d^{-1}$)	Liss and Merlivat Hg^o Flux ($pmol\ m^{-2}\ d^{-1}$)	Wanninkhof Hg^o Flux ($pmol\ m^{-2}\ d^{-1}$)	Asher et al. Hg^o flux ($pmol\ m^{-2}\ d^{-1}$)
Winter (Feb 1996)	0.48	1.34	3.51	75	210	550
Spring (May 1997)	1.76	3.30	4.09	180	340	390
Summer (Aug 1995)	0.17	1.38	3.28	64	520	1230
Fall (Oct 1996)	0.83	2.53	3.70	170	530	780
Fall (Oct 1997)	0.18	1.47	3.31	8	68	150
LIS Flux ($kg\ yr^{-1}$)				**24**	**80**	**155**

Wind data are 15-min interval measurements from the top of the UCMS building at Avery Point, Groton, CT (courtesy of M. M. Howard–Strobel). Atmospheric total gaseous Hg (TGM; exists as >99% Hg^o) values are based upon the 1993–1995 data set compiled by K. Rolfhus at the University of CT Avery Point Campus (unpublished). DGM data from stations along LIS central axis only.

Therefore, it is used as an "upper bound" estimate for the gas exchange flux.

Elemental Hg flux is then determined by using the following equation:

$$Hg^o \text{ Flux to Atm.} = k[Hg^o_{LIS} - Hg^o_{EQ}]$$

where Hg^o_{LIS} is the measured DGM concentration and Hg^o_{EQ} is the Hg^o concentration calculated to be in atmospheric equilibrium at a given temperature, salinity, and total gaseous Hg concentration (see the Section 2.4. and Table 5; Wanninkhof, 1992; Broecker and Peng, 1982).

Wind speed was averaged from 15-min. measurements on the roof of the UConn Marine Sciences Building (Groton, CT; M. M. Howard–Strobel), whereas water temperature and salinity were obtained from the CT DEP Water Quality Program (Olsen, personal communication). Atmospheric TGM (>99% Hg^o) estimates were made based upon measurements taken at the Avery Point Campus lighthouse, averaged weekly from 1993 to 1995 (unpublished data). A summary of the seasonal model parameters is listed in Table 5.

The average seasonal flux values using the Wanninkhof model was 342 pmol $m^{-2}\ d^{-1}$, 103 pmol $m^{-2}\ d^{-1}$ for Liss and Merlivat, and 660 pmol $m^{-2}\ d^{-1}$ for Asher et al., corresponding to an annual average range of 120 to 775 moles $Hg^o\ yr^{-1}$ (24–155 kg yr^{-1}) when integrated over the area of LIS ($3.2 \times 10^9\ m^2$). These flux results are consistent with literature values from a wide variety of environments, including the Chesapeake Bay Estuary [130 pmol $m^{-2}\ d^{-1}$, Mason et al. (1999)], the North Sea [59–1110 pmol $m^{-2}\ d^{-1}$, Baeyens and Leermakers (1998)], the Equatorial Pacific [160–1440 pmol $m^{-2}\ d^{-1}$, Mason and Fitzgerald (1993)], and freshwater lakes in Wisconsin [57–274 pmol $m^{-2}\ d^{-1}$, Vandal et al. (1991)].

Prior gas exchange modeling studies have reported that k varies (on average) as the square of wind speed, with a range of $u^{1.5}$ to $u^{2.2}$ (Hartman and Hammond, 1985; Broecker et al., 1985). The three gas exchange models used here report a wide range of fluxes for LIS. The Liss and Merlivat model utilizes a series of linear relationships related to mean wind speed u (derived from SF_6 in fresh waters), but the slopes are a factor of two lower than that found in comparable wind tunnel studies (Liss and Merlivat, 1986). Such results may be due to differences in wind fetch and surfactants between field and laboratory conditions. Recent investigation (Wanninkhof and McGillis, 1999) has suggested a cubic relationship between short-term wind speeds and gas exchange. This is characterized by diminished transfer at low wind speeds (0–11 m s^{-1}) relative to Wanninkhof (1992) due to the possible impacts of surfactants, and by substantially greater transfer above 11 m s^{-1}. Additional model validation is necessary, as low solubility gases such as SF_6 and ^3He exhibit significantly lower transfer velocities at high winds than are predicted by the CO_2-parameterized cubic model.

Estimates of gas evasion based solely on wind speed data have several inherent sources of uncertainty, including interface turbulence, assumptions regarding Hg^o diffusivity, and Schmidt number. Turbulence at the air/sea interface is likely governed by processes such as bubbles, surfactants, boundary layer stability, and wind fetch, some of which may not be significantly related to surface winds (Asher and Wanninkhof, 1998). Empirical wind speed-gas transfer relationships vary widely between studies (see above references). Recent literature has noted the potential effects of interface temperature disequilibrium, which may result in diel flux variations as great as 44% that are not related to the geochemistry of Hg (Loux, 2000). Due to these current uncertainties, we discuss the Wanninkhof (1992) derived fluxes relative to the budgets of LIS and other systems below.

Wanninkhof (1992) states that there is 30% uncertainty in the $^{14}CO_2$ model parameterization; when combined with the ~9% relative standard error of the measurements, a final uncertainty of 32% is reported (the geometric mean of the two sources of error). Comparison of the Wanninkhof Hg^o flux

(80 ± 25 kg yr^{-1}) was made to other inputs/output estimates from the LIS budget of Fitzgerald et al. (in press); these included contributions from watersheds, direct deposition, and WTFs, as well as the removal processes of sedimentation and tidal mixing. Elemental Hg evasion is an important export term when compared to the magnitude of the inputs; this export term constitutes ~35% of the total inputs to LIS, and 300% that of direct Hg deposition (Fitzgerald et al., in press). This value is similar to that estimated by Mason et al. (1994) for Hg^o evasion from oceans compared to the global cycle (10 Mmol yr^{-1}; 30%), and that of Lake Michigan (40%; Mason and Sullivan, 1997).

Although a halving or doubling of the Hg^o flux is significant geochemically, the importance of volatilization cannot be ignored; 32% uncertainty in the Wanninkhof (1992) flux widens the range of the flux estimate to 55 to 105 kg yr^{-1}, which corresponds to 24 to 45% of the inputs in the LIS budget. Thus, LIS may be considered an "incubator" for Hg(II) substrate that enters via rivers, WTF's, and direct deposition. Further, LIS removes a significant fraction of Hg from coastal waters that might otherwise have been incorporated in the food web (as MeHg) or sediments. In this sense, LIS may be thought of as an extension of the terrestrial system, where similar processes (such as volatilization from soil; Capri et al., 1997) are occurring. Comparisons of mean areal anthropogenic Hg emissions from the contiguous United States (18 g km^{-2} yr^{-1}; estimated from 144 metric tons [U.S. EPA, 1998b] divided by area of U.S. landmass) are similar to that estimated for LIS (25 g km^{-2} yr^{-1}), which supports this contention.

Waste water treatment facility inputs to LIS may lead to competing processes with regards to DGM, where particulate and dissolved organic matter loading serve to make Hg less labile, and yet supply large quantities of potentially reducible Hg(II). The surficial DGM and filtered Hg_R data do not indicate a distinct signature related to enhanced organic material loading (particularly in western LIS), which suggests that WTFs may not play a direct role in supplying reactant for Hg^o production. Processes that convert bound Hg(II) to more labile species may result in elevated Hg^o production rates; more data is required to establish these relationships.

4. CONCLUSION

It is apparent from the seasonal surveys that DGM varies substantially in both time and space, and that there may be significant annual variability associated with the wind field history, Hg(II) inputs, solar radiation, and biological activity.

The distribution of Hg_T and Hg_R indicates that particle scavenging of the metal is an important geochemical process, especially in western LIS. Further, the distribution of Hg_R, % Hg_R, and the filtered Hg_R/DOC relationship suggests that DOM is a principal mediator of Hg lability, and by extension, DGM production. This study presents a limited data set linking these processes together. A more complete exploration of these relationships is required, especially with regards to physical/chemical characterization of DOC and its specific controls over Hg lability.

Estimates of Hg^o volatilization to the atmosphere were calculated using three empirical gas-exchange models applied to open-ocean waters. The integrated evasional value (Wanninkhof, 1992) for LIS was 80 ± 25 kg yr^{-1}, a flux that is equivalent in magnitude to 35% of total inputs and over three times that of direct deposition. These scaling exercises demonstrate that Hg^o evasion from surface waters is an important geochemical process in the coastal waters of LIS. We suggest that a similar relationship holds for other coastal systems with significant loadings of Hg from terrestrial and atmospheric sources.

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